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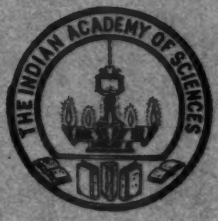

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ANOMALOUS DISPERSION METHOD OF DETERMINING STRUCTURE AND ABSOLUTE CONFIGURATION OF CRYSTALS

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(Communicated by Dr. G. N. Ramachandran, F.A.SC.)

Abstract

It is possible to determine the phases of structure factors of a non-centro-symmetric crystal from an experimental measurement of the intensity-differences between pairs of inverse reflections, produced by anomalous dispersion. But the determination is ambiguous. An interesting possibility arises when the group of anomalous scatterers possesses a centre of inversion. It is found that in this case, a Fourier synthesis calculated by using both the possible values of the phase angle will contain, in addition to the peaks of the real structure, an equal number of negative peaks at positions related to the former by inversion about the inversion-centre of the group of anomalous scatterers. This idea has been used to determine the absolute configuration of L-ephedrine hydrochloride.

1. Introduction

During recent years the anomalous dispersion effect has been increasingly used by many workers to determine the absolute configuration of a number of crystals. In all the cases, the structures had to be solved beforehand by conventional methods of X-ray crystal structure analysis (which give only the structure and not the configuration) and the anomalous dispersion effect was used only to determine the configuration of the structure. However, the effect can be put to far greater use than mere determination of the configuration. In a recent paper (Ramachandran and Raman, 1956), it has been shown that it is sometimes possible to determine both the structure and the absolute configuration of a non-centrosymmetric crystal in a straightforward way by making full use of the effect of anomalous dispersion. It is found that the phases $\alpha(hkl)$ of the structure factors $F'(hkl)$ can be determined, but for an ambiguity, from an experimental measurement of the intensity differences between pairs of inverse reflections hkl and $\bar{h}\bar{k}\bar{l}$, produced by the imaginary component $\Delta f''$ of the atomic sacttering factors. The nature of the ambiguity as well as methods for its resolution have been

discussed and the validity of the method was also tested in the case of the alkaloid, L-ephedrine hydrochloride. The phase angles determined by the anomalous dispersion method were found to agree very well with those calculated from known atomic co-ordinates. In this paper, further results which tend to confirm the various conclusions previously arrived at are reported. The absolute configuration of L-ephedrine hydrochloride, which has been determined by an interesting application of the new method, is also presented.

2. Phase Determination from Anomalous Dispersion

The basic theoretical relations have already been derived in the earlier paper and only a short account is given here so as to make this paper self-contained. Let the crystal contain one atom or a set of p crystallographically equivalent atoms A for which the imaginary component $\Delta f''$ is significant, while for the rest, R, of the structure (N $-$ p atoms) this component is negligible. Let $\mathbf{F}_A'$ and $\mathbf{F}_A''$ denote the contributions from the real and imaginary parts of the scattering factors of atoms A and let $\mathbf{F}_R$ denote the contribution from the atoms R. These vectors are shown in Figs. 1 (*a*) and 1 (*b*) for both the reflection *hkl* and its inverse $\bar{h}\bar{k}\bar{l}$. (In the latter case, the vectors are represented by a bar over the symbols.) From these figures it is clear that

$$|\mathbf{F}|^2 = |\mathbf{F}'|^2 + |\mathbf{F}_A''|^2 + 2|\mathbf{F}'|\,|\mathbf{F}_A''|\cos\theta \qquad (1)$$

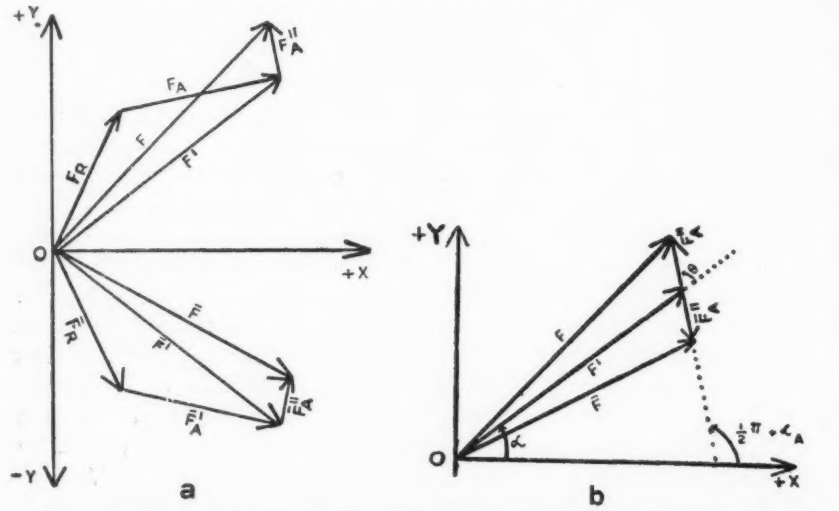

FIG. 1. Diagram showing the different components of the structure factors F and $\bar{\mathbf{F}}$.

and

$$|\bar{\mathbf{F}}|^2 = |\mathbf{F}'|^2 + |\mathbf{F}_A''|^2 - 2|\mathbf{F}'|\,|\mathbf{F}_A''|\cos\theta \tag{2}$$

whence

$$\begin{aligned}\Delta|\mathbf{F}|^2 &= |\mathbf{F}|^2 - |\bar{\mathbf{F}}|^2 \\ &= 4|\mathbf{F}'|\,|\mathbf{F}_A''|\cos\theta\end{aligned} \tag{3}$$

where θ is the angle between the vectors $\mathbf{F}'$ and $\mathbf{F}_A''$. It is obvious that $\mathbf{F}'$ is the structure factor when the anomalous dispersion effect is zero. If α be the phase of $\mathbf{F}'$ and α_A the phase of $\mathbf{F}_A'$ then,

$$\alpha = \tfrac{1}{2}\pi + \alpha_A - \theta. \tag{4}$$

Equations (3) and (4) may be used to determine α from experimentally measured $\Delta|\mathbf{F}|^2$ provided the positions of the anomalous scatterers A are known. It is not difficult to know the latter, since the anomalous scatterers are also usually heavy atoms.

But there is an ambiguity in the determination. This ambiguity arises because θ derived from cos θ [equation (3)] may be positive or negative and correspondingly there are two values possible for α, given by

$$\alpha_{1,2} = \tfrac{1}{2}\pi + \alpha_A \pm \theta. \tag{5}$$

3. The "Anomalous" Synthesis

It is interesting to investigate the nature of the Fourier synthesis in which both the possible values, α_1 and α_2, obtained by the anomalous dispersion method, are used. This synthesis may be called the "anomalous" synthesis: $\rho_{an}(xyz)$. It is given by

$$\begin{aligned}\rho_{an}(xyz) = \frac{1}{2V}\sum_h\sum_{-\infty}^{+\infty}\sum_l |\mathbf{F}'(hkl)|\{&\exp i\alpha_1(hkl) \\ &+ \exp i\alpha_2(hkl)\}\exp -2\pi i(hx+ky+lz)\end{aligned} \tag{6}$$

and the two values of α are related by

$$\alpha_2 = 2\alpha_A + \pi - \alpha_1. \tag{7}$$

In general, the synthesis (6) may be shown to contain peaks at the correct atomic positions, in addition to a background which may contain spurious peaks. An interesting possibility arises in the special case when the group of anomalous scatterers possesses a centre of inversion. In this case,

the value of α_A is 0 or π and the two possible values of the phase angles are α and $(\pi - \alpha)$. If both these values are used, the resulting synthesis is simply the Fourier sine synthesis ρ_s, and is given by

$$\rho_{an}(xyz) = \rho_s(xyz) = \frac{2}{V} \sum_{0}^{\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} | F'(hkl) | \sin \alpha (hkl) \times \sin 2\pi (hx + ky + lz) \quad (8)$$

This synthesis may be shown to contain, in addition to the positive peaks of the true structure, an equal number of negative peaks at positions related to the former by inversion at the inversion-centre of the group of anomalous scatterers. The proofs for both the cases will be given later.

Thus it is possible to determine the structure and absolute configuration from the anomalous synthesis. However it is to be noted that the anomalous synthesis will give no information about those parts of the structure which by accident happen to be centrosymmetric about the inversion-centre of the anomalous group. In such cases it is necessary to use a certain amount of care and judgment and confirm the deductions with other methods like the heavy atom method suggested in Section 5.

This method of determining the structure in its absolute configuration seems even more promising than the method of Pepinsky and Okaya (1956) using the Patterson sine synthesis (P_s). These authors have investigated the nature of the Patterson function obtained from the intensity data alone when some of the atoms are anomalous scatterers. It is found that both the structure and absolute configuration can be derived from the imaginary part $P_s(xyz)$ of the complex Patterson function. However the interpretation of the Patterson sine synthesis is much more difficult than that of the Fourier sine synthesis. This is obvious from the fact that, whereas the latter consists of only the structure and its negative inverse, the P_s-function will consist of a series of p images of the structure as seen from each one of the p atoms in the set A and will contain, in addition, a duplicate of the entire series in the form of negative peaks by inversion at the origin of the diagram.

4. Comparison of the "Anomalous" and the "Isomorphous" Synthesis

It is interesting to compare the superposed synthesis obtained with the anomalous dispersion method with a similar synthesis which may be obtained in the parallel case of phase determination by the isomorphous replacement

technique. In this case also the phase determination is ambiguous and the two solutions α_3 and α_4 obtained for α are related by

$$\alpha_4 = 2\alpha_A - \alpha_3, \tag{9}$$

where α_A is the phase of the contribution from the group of replaceable atoms. The Fourier synthesis obtained by using both the solutions may be called the "isomorphous synthesis," $\rho_{is}(xyz)$, and is given by

$$\rho_{is}(xyz) = \frac{1}{2V} \sum_h \sum_{-\infty}^{+\infty} \sum_l |F'(hkl)| \{\exp i\alpha_3(hkl) + \exp i\alpha_4(hkl)\} \exp -2\pi i(hx + ky + lz) \tag{10}$$

As in the case of the anomalous synthesis, this synthesis also will give peaks at the correct atomic positions in addition to a background. In the case when the group of replaceable atoms possesses a centre of inversion, the two solutions are α and $-\alpha$ and the isomorphous synthesis calculated using both the possible values becomes merely the Fourier cosine synthesis (ρ_c say).

$$\rho_{is}(xyz) = \rho_c(xyz) = \frac{F(000)}{V} + \frac{2}{V} \sum_0^{\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} |F'(hkl)| \times \cos\alpha(hkl) \cos 2\pi(hx + ky + lz). \tag{11}$$

It can be shown that this ρ_c function will contain two sets of peaks, both positive and the two sets will be related by inversion about the inversion-centre of the group of replaceable atoms. Thus ρ_{is} will give the structure and its positive inverse whereas ρ_{an} will give the structure and the negative inverse.

Obviously a happy example is one where the replaceable atoms are also anomalous scatterers. Then the isomorphous method can be used to determine values of α and $-\alpha$ and the anomalous dispersion method determines values of α and $(\pi - \alpha)$. Using both methods in conjunction it is possible to fix uniquely the value of α and calculate the electron-density,

$$\rho(xyz) = \frac{F(000)}{V} + \frac{2}{V} \sum_0^{\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} |F'(hkl)| \cos\alpha(hkl) \times \cos 2\pi(hx + ky + lz) + \frac{2}{V} \sum_0^{\infty} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} |F'(hkl)| \sin\alpha(hkl) \times \sin 2\pi(hx + ky + lz). \tag{12}$$

Thus the two methods are complementary. The isomorphous replacement method determines the first synthesis given by equation (12) (*i.e.*, the structure and its positive inverse) and the anomalous dispersion method determines the second synthesis (*i.e.*, the structure and its negative inverse) and the two together add up to give the electron-density ρ (xyz) (*i.e.*, the structure).

It is also interesting to note that both methods are based on more or less the same principle, that phase determination is possible by introducing a change in the scattering powers of a few atoms and studying its effect on the intensities of the X-ray reflections. In the isomorphous replacement method, this change is achieved by isomorphously replacing some of the atoms. In the anomalous dispersion method there is no replacement as such, but use is made of the fact that when anomalous dispersion takes place, the intensities of the inverse reflections hkl and $\bar{h}\bar{k}\bar{l}$ are different. The phases are determined from the intensity differences between pairs of inverse reflections. Thus in this case the isomorphous substances appear to be merely the structure and its inverse and the analogy is clearer if it is remembered that the reflection hkl of the structure is the reflection $\bar{h}\bar{k}\bar{l}$ of the inverse.

Between the two methods, preference should be given to the anomalous dispersion method because it requires only one crystal, whereas the other method demands a series of isomorphous substances, with a minimum of at least two.

5. EXPERIMENTAL VERIFICATION

The method has been experimentally verified in an investigation of the structure of L-ephedrine hydrochloride. The structure of this compound has been determined by conventional methods (Phillips, 1954). Our aim was to test the new method both as regards the determination of phase and the determination of absolute configuration. The crystal belongs to the monoclinic space group and the unit cell contains two chlorine atoms. These show a measurable, though small, anomalous effect ($\triangle f''_{Cl} = 0{\cdot}69$) even for CuK$\alpha$ radiation. The crystals are elongated along the b-axis but the $h0l$ reflections are not useful for our purpose. Therefore it was necessary to make measurements in the c-zone. The differences in the intensities of the pairs of inverse reflections $hk0$ and $\bar{h}\bar{k}0$ were measured with a Geiger counter spectrometer. The measurements were put on an absolute basis by direct comparison with the reported values of $\mathbf{F_c}$. The values of α and

$(\pi - \alpha)$ were obtained by using an approximate form of expression (3), namely,

$$\sin \alpha = \Delta \mid \mathbf{F} \mid / 2\,\mathbf{F}_{\mathrm{A}}'',$$

which is valid if $\mathbf{F}_{\mathrm{A}}'' \ll \mathbf{F}_{\mathrm{A}}'$. The phase angles thus derived were found to be in good agreement with the correct values calculated from the atomic co-ordinates. The measurements were also put on an absolute basis by the method of Wilson (1942) which is the usual method adopted when the structure is not known. The phase angles derived in this way were not much different from the above values. A table showing the phase angles derived by the former method and the correct values has been given in the earlier paper (Ramachandran and Raman, 1956).

Using these values and the observed values of $\mid \mathbf{F}_0 \mid$ the ρ_{an}-synthesis was calculated (Fig. 2). The phases of some of the reflections could not be determined because the contribution from the chlorine atoms to these reflections is zero. The corresponding coefficients had to be dropped from the

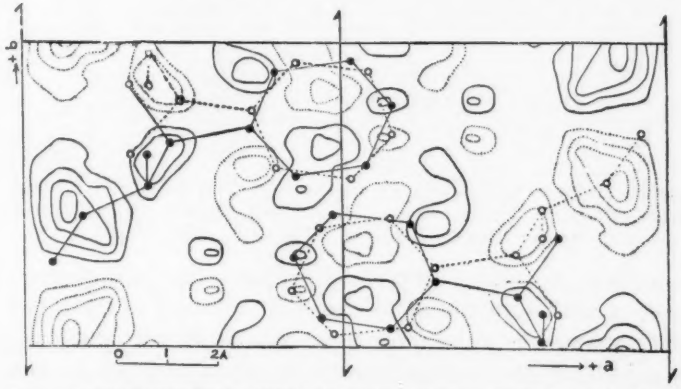

FIG. 2. ρ_{an}-function projected on (001) using values of phase angles found by the anomalous dispersion method. Contours have been drawn at arbitrary intervals of 20. The full lines represent positive contours and broken lines represent negative contours.

synthesis. Further, the phases of a few reflections disagreed by more than twenty degrees from the correct phases calculated from known atomic co-ordinates. In spite of this, these were included in the synthesis, as this is what one would do if the phases were not known to start with. To see what would be the effect of both these defects, the synthesis was calculated using the correct values of α and $(\pi - \alpha)$ taken from Phillips' paper and this is shown in Fig. 3. It is found that the two diagrams agree in their broad

features, though the latter is in better agreement with the correct structure. In interpreting the diagrams, the important fact should be borne in mind that the positive and the negative density distributions are superposed and will interfere. This effect will be more serious in a two-dimensional projection than in a three-dimensional synthesis. To see the nature of this interference, the two molecules are drawn in both the diagrams, using the atomic co-ordinates given by Phillips and their negative inverses have also been drawn. If now the phases are calculated, taking only the positions of the positive peaks then the ambiguity in the solution of α may be resolved.

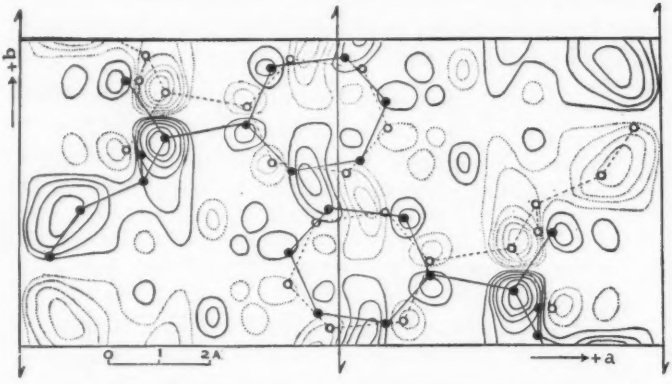

FIG. 3. ρ_{an}-function projected on (001) using correct values of the phase angles. The contours have been drawn at arbitrary intervals of 20. The full lines represent positive contours and broken lines represent negative contours.

It may be resolved in another way also (Ramachandran and Raman, 1956). Of the two possible values of α, the one which is nearer to the phase of the chlorine atoms may be chosen for a preliminary Fourier synthesis. This procedure is justified for those reflections for which the contribution from the heavy chlorine atoms is fairly large. This synthesis is shown in Fig. 4, which is seen to be a good approximation to the structure. This use of the heavy atom method has been suggested by Peerdemann and Bijvoet also (1956).

6. INDEXING THE REFLECTIONS FOR FINDING ABSOLUTE CONFIGURATION

The ρ_{an}-diagram can be used to determine the absolute configuration of the compound. The positive peaks of the diagram correspond to the structure in its absolute configuration provided correct signs have been assigned to the indices $hk0$. This is easily done by choosing a particular co-ordinate system on the crystal and indexing the reflections on the basis of this system.

We have conventionally taken this frame of reference to be a right-handed system of co-ordinates. For a monoclinic crystal, the senses of the co-ordinate axes can be chosen in two equivalent ways to get a right-handed system, as shown in Figs. 5 (*a*) and 5 (*b*). The sense of either the *c*- or *a*-axis can be arbitrarily chosen and then the senses of the other two axes are automatically fixed by the following two stipulations:—

(*a*) The angle between the positive directions of *c*- and *a*-axes should be obtuse; this fixes the sense of *a*, once the sense of *c* has been arbitrarily chosen;

(*b*) The sense of *b* is fixed by the fact that the three axes should form a right-handed system.

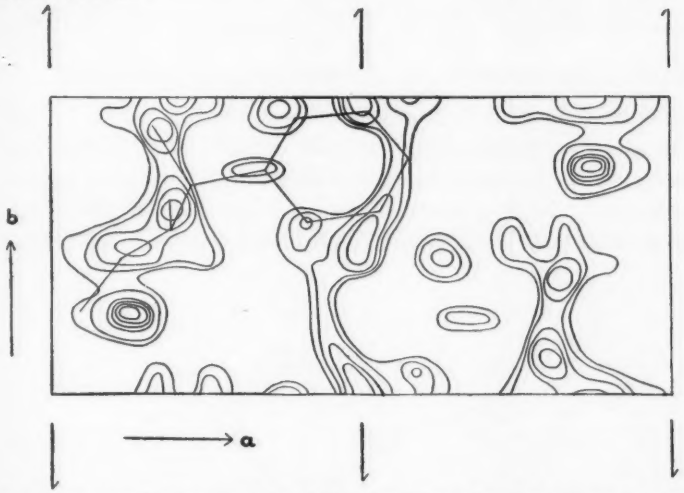

FIG. 4. Electron-density projected on (001). Contours have been drawn at intervals of approximately 1 *e*. A^{-2} except near the chlorine atom where the interval is 2 *e*. A^{-2}. The one electron contour is not shown.

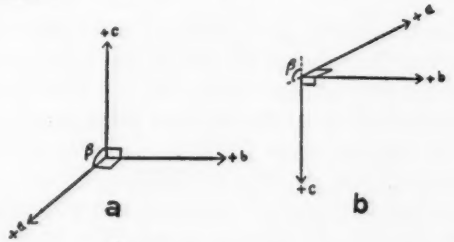

FIG. 5. The two equivalent right-handed co-ordinate systems possible for monoclinic crystals.

In the particular example, the crystal was set with the *c*-axis vertical. The directions of *a*- and *b*-axes were determined from the known positions at which the corresponding planes (100) and (010) reflect in the spectrometer. The positive direction of *c* was arbitrarily chosen to be vertically upwards. The sense of *a* can then be fixed from stipulation (*a*) provided it is known whether the chosen direction of *a* makes an obtuse or an acute angle with the chosen *c* direction. This point was decided by studying the direction of shift of the higher layer spots of an oscillation-photograph taken about the *c*-axis. The sense of the remaining axis, namely *b*-axis, can be fixed from stipulation (*b*). This procedure of assigning correct signs to the indices is essential, for a reversal in the sign will lead to the inverse configuration. Some aspects of the method of assigning the indices correctly in an orthorhombic crystal have been discussed by Peerdemann and Bijvoet (1956).

7. Absolute Configuration of L-Ephedrine Hydrochloride

The absolute configuration of L-ephedrine hydrochloride has thus been determined (Fig. 6). The alkaloid ephedrine $C_6H_5CH\,(OH)\,CH\,(CH_3)NH\,CH_3$ has four isomers, namely, (−)-ephedrine, (+)-ephedrine, (−)-psi-ephedrine and (+)-psi-ephedrine. Their conformations have been studied by stereochemical methods (Henry, 1949; Close, 1950) and relative configurations have

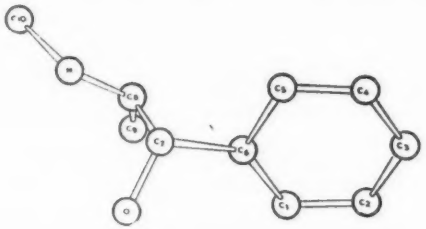

FIG. 6. Absolute configuration of L (+)-ephedrine molecule.

been assigned to the isomers from their relation, established by chemical means, to D-glyceraldehyde and hence to D-tartaric acid whose absolute configuration is now known (Bijvoet and others, 1951). The present analysis gives an independent determination of the absolute configuration of L-ephedrine hydrochloride. The configuration found by us is the one assigned to (+)-ephedrine. The earlier X-ray analysis of Phillips did not make use of the effect of anomalous dispersion and so it is consistent with this configuration as well as its mirror-image. Of the two possibilities Phillips chose the configuration which was in agreement with the one deduced by a number

of chemical workers as the correct configuration. The present analysis confirms this choice.

The author wishes to express his deep indebtedness to Professor G. N. Ramachandran for the guidance and encouragement throughout this investigation.

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THE ENUMERATION OF POSITIVE RATIONAL NUMBERS

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§1. Introduction

The aim of this paper is to indicate a method of enumeration of positive rational numbers. Such an enumeration consists in establishing a $(1-1)$ correspondence between the elements of the set R^+ of positive rationals (or a subset of it) and those of the set I^+ of positive integers. A few methods of enumeration of rationals have been indicated in Wilder[4] (pp. 80–81, 106–107).

In the following, we shall also study some of the properties of the median series (defined below) which is akin to the Farey series and also about the τ-function defined by Hermes.[1] We make use of the properties of the median series and the τ-function to enumerate the positive rationals > 1.

Hermes, on the basis of his τ-function, proves certain results which, we are bound to think, are motivated by the structure of the median series studied in the paper. However Hermes does not obtain all the results obtained here and in particular Hermes does not interpret the binary scale representation of an integer n in relation to the structure of the median series.

Hermes' paper was as a matter of fact suggested by a paper of Stern[2] in which he introduces the series called the Stern's series

$$S_0 \ldots \quad (r, s)$$

$$S_1 \ldots \quad (r, r+s, s)$$

$$S_2 \ldots \quad (r, 2r+s, r+s, r+2s, s)$$

and so on. If $r = 0$, $s = 1$ in S_i then this series becomes identical with the numerator of the median series M_i. If $r = 1$, $s = 0$, the series becomes identical with the denominator of M_i. From our point of view the importance of Stern's series is subordinate to that of the median series.

The significance of the partial quotients in the division transformation for two numbers a and b relatively prime, is also brought out in terms of the median approximations defined in Section 5. These approximations

are also the approximations of Vahlen[3] but they differ from those of Vahlen in the method of introduction. While Vahlen introduces the approximations to a real number ρ in connection with Farey series and is able to prove the important result that the approximations can be arranged in a single series $a_1, a_2, a_3, \ldots\ldots\ldots$ so that a_i, a_{i+1} are the two consecutive terms of F_i, the Farey series of i-th order, between which the real number ρ lies, we however define the same approximations in relation to the structure of the median series and Vahlen's series arrangement is no longer true for the median approximations defined by us. The relation between the Farey series and median series do not seem to be fully known though we can show that the Farey series F_i is a part of the median series M_i but not a part of M_{i-1}. The latter part is evident since the terms $1/i$ belong to M_i but not to M_{i-1}. To prove that $F_i \subset M_i$ we can use the following result which can be easily proved: "The sum of the partial quotients of a rational number m/n in lowest terms is equal to or less than the greater of m and n."

Hermes' τ-function is introduced here in Section 6 specifically by means of the order in M_i and the recurrence relations on which Hermes bases his definition of the τ-function are directly deduced in Section 6, from the order properties of the median series.

The results in Sections 5 and 6 are believed to be new. The auxiliary properties of medians, necessary for proving them, have been collected in Section 4.

I am indebted to Dr. R. Vaidyanathaswamy for his guidance and to Mr. S. Swetharanyam for his help in preparing this paper in its final form.

§2. Notations and Definitions

2.1. The τ-function of Hermes is defined by the recurrence relation

$$\tau_1 = 1 \text{ and } \tau_n = \tau_{(n-2^\nu)} + \tau_{(2^{\nu+1}+1-n)}$$

where $2^\nu < n \leq 2^{\nu+1}$.

2.2. The Gaussian bracket is defined by (2.1.1)

$$[\ ] = 1, \qquad [a] = a \text{ and}$$

$$[a, \beta, \ldots., \gamma, \delta, \epsilon, \eta, \ldots., \zeta] \tag{2.2.1}$$

$$= [a, \beta, \ldots., \partial]\,[\epsilon, \eta, \ldots.\zeta] + [a, \beta, \ldots., \gamma]\,[\eta, \ldots., \zeta].$$

2.3. If any positive integer n has the unique alternating binary scale expansion

$$n = 2^{a_0} - 2^{a_1} + 2^{a_2} - \ldots\ldots\ldots + 2^{a_\lambda}, \tag{2.3.1}$$

$(0 \leqslant a_0 < a_1 < a_2 < \ldots < a_\lambda)$ with odd number of terms (*i.e.*, λ even), then

$$\tau_n = \tau\,(a_0, a_1 - a_0, a_2 - a_1, \ldots, a_\lambda - a_{\lambda-1}) \tag{2.3.2}$$

$$= (1 + a_0, a_1 - a_0, a_2 - a_1, \ldots, a_\lambda - a_{\lambda-1}) \tag{2.3.3}$$

[*vide* Hermes[1] (satz 1)]. The fact that the alternating binary scale expansion is unique for a given integer and that there are an odd number of terms in such an expansion is true for $n = 1, 2, 3$ for, $1 = 2^\circ$, $2 = 2^1$, $3 = 2^\circ - 2^1 + 2^2$. Let us now assume that this is true for all integers less than N (say) where $2^{k-1} < N \leq 2^k$. Now N can be uniquely written in the form

$$N = 2^{k-1} + 2^{a_1} + 2^{a_2} + \ldots + 2^{a_n}$$

where $k - 1 > a_1 > a_2 > \ldots > a_n \geq 0$. (2.3.4)

Let now the alternating binary scale expansion of $N - 2^{k-1}$ be

$$N - 2^{k-1} = 2^{a_1+1} - 2^b + \ldots \quad \text{(odd number of terms)}$$

Then

$$N = 2^{k-1} + 2^{a_1+1} - 2^b + \ldots \quad \text{(even number of terms)}$$

$$= 2.2^{k-1} - 2^{k-1} + 2^{a_1+1} - 2^b + \ldots$$

$$= 2^k - 2^{k-1} + 2^{a_1+1} - 2^b + \ldots \quad \text{(odd number of terms).}$$

This is an alternating binary scale representation of N with an odd number of terms and this is unique because (2.3.4) is unique.

2.4. The Median series is defined as follows:

$$M_0 = \left(\frac{0}{\bar{1}}, \frac{1}{\bar{0}}\right)$$

$$M_1 = \left(\frac{0}{\bar{1}}, \frac{1}{\bar{1}}, \frac{1}{\bar{0}}\right)$$

$$M_2 = \left(\frac{0}{\bar{1}}, \frac{1}{\bar{2}}, \frac{1}{\bar{1}}, \frac{2}{\bar{1}}, \frac{1}{\bar{0}}\right)$$

$$M_3 = \left(\frac{0}{\bar{1}}, \frac{1}{\bar{3}}, \frac{1}{\bar{2}}, \frac{2}{\bar{3}}, \frac{1}{\bar{1}}, \frac{3}{\bar{2}}, \frac{2}{\bar{1}}, \frac{3}{\bar{1}}, \frac{1}{\bar{0}}\right)$$

and so on.

§3. Division Transformation and Euclidean Algorithm

It is known that given any two positive integers a and b, an Euclidean algorithm can be constructed in the form

$$\begin{aligned}
a &= ba_0 + b_0 && (0 \leq b_0 < b)\\
b &= b_0a_1 + b_1 && (0 \leq b_1 < b_0)\\
b_0 &= b_1a_2 + b_2 && (0 \leq b_2 < b_1)\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
b_{n-3} &= b_{n-2}\,a_{n-1} + b_{n-1} && (0 \leq b_{n-1} < b_{n-2})\\
b_{n-2} &= b_{n-1}\,a_n && (a_n > 1) \qquad (3.1)
\end{aligned}$$

which ultimately yields the Greatest Common Divisor (hereafter denoted as (GCD) of a and b. The numbers $a_0, a_1, a_2, \ldots, a_n$ which appear in the successive stages of the division transformation are called the partial quotients in the Euclidean algorithm. It is also known that the rational a/b can be put in the form of a regular finite continued fraction (hereafter denoted as CF)

$$\frac{a}{b} = c_0 + \frac{1}{c_1} + \frac{1}{c_2} + \cdots\cdots + \frac{1}{c_n}. \qquad (3.2)$$

The numbers $c_0, c_1, c_2, \ldots$ are called the partial quotients of the continued fraction. It is easily seen that the equations

$$a_i = c_i \qquad (i = 0, 1, 2, 3, \ldots, n)$$

are true; that is, the partial quotients obtained in the above two operations are respectively the same.

The number of partial quotients can always be made odd; for if it is even, then a_n can be replaced by the two partial quotients $(a_{n-1}, 1)$ so that the CF becomes

$$\frac{a}{b} = a_0 + \frac{1}{a_1} + \frac{1}{a_2} + \cdots + \frac{1}{a_{n-1}} + \frac{1}{1}.$$

In (3.1) b_{n-1} is the GCD of a and b. The remainders $b_0, b_1, b_2, \ldots, b_{n-2}$ at each stage of the operation can be eliminated in terms of $a_0, a_1, a_2, \ldots, a_n$ and b_{n-1} and then we get

$$\begin{aligned}
b_{n-2} &= b_{n-1}\,a_n\\
b_{n-3} &= b_{n-1}\,[a_{n-1}, a_n]\\
b_{n-4} &= b_{n-1}\,[a_{n-2}, a_{n-1}, a_n]\\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\\
b_0 &= b_{n-1}\,[a_2, a_3, \ldots, a_n].
\end{aligned}$$

Finally we have

$$b = b_{n-1}\,[a_1, a_2, a_3, \ldots, a_n]$$

and

$$a = b_{n-1}\,(a_0, a_1, a_2, \ldots, a_n) \tag{3.3}$$

Since b_{n-1} is the GCD of a and b, it follows that

the integers represented by the two Gaussian brackets in (3.3) are relatively prime. (3.4)

The result of the elimination is also the expression of a/b as the regular finite continued fraction

$$\frac{a}{b} = a_0 + \frac{1}{a_1} + \frac{1}{a_2} + \ldots + \frac{1}{a_n}$$

$$= \frac{[a_0, a_1, a_2, \ldots, a_n]}{[a_1, a_2, a_3, \ldots, a_n]}.$$

It follows that if a/b is in its lowest terms

$$a = [a_0, a_1, a_2, \ldots, a_n]$$

$$b = [a_1, a_2, a_3, \ldots, a_n]. \tag{3.5}$$

From the above we see that the positive rational $\mathbf{R} = a/b$ can be made to correspond to a sequence of integers $a_0, a_1, \ldots, a_n$ ($a_0 \geq 0$, $a_i > 0$ for $i = 1, 2, 3, \ldots, n$) which are the partial quotients in the CF expansion of $\mathbf{R}$ and these partial quotients completely specify the rational number. If $a/b > 1$ (so that $a_0 \geq 1$) is in its lowest terms, then the reverse of the CF is equal to another rational number

$$\mathbf{R}' = \frac{[a_n, a_{n-1}, \ldots, a_1, a_0]}{[a_{n-1}, a_{n-2}, \ldots, a_1, a_0]}$$

$$= \frac{p_n}{p_{n-1}}$$

where p_n is the numerator of the n-th convergent of the original CF. We can call $\mathbf{R}'$ as the associate of $\mathbf{R}$. It is clear that the relation between a rational number and its associate is symmetrical.

Therefore we obtain that if $a_i \geq 1$ ($i = 0, 1, 2, \ldots, n$)

$$[a_0, a_1, \ldots, a_n] = [a_n, a_{n-1}, \ldots, a_1, a_0]. \tag{3.6}$$

With any rational number $R = a/b$ we shall associate the function $\sigma(R) =$ the sum of the partial quotients in the CF development of R; *i.e.*,

$\sigma(R) = a_0 + a_1 + \ldots + a_n$. If R and R′ are associates, then $\sigma(R) = \sigma(R')$. The significance of this function is brought out later on.

§4. The Median and the Elementary Properties of the Median Series

We define the median of two positive rationals a/b and c/d (in lowest terms) to be $(a + c)/(b + d)$. Some of the important properties of the median are

4.1.1. The median m_1/m_2 of two unequal positive rationals a/b and c/d lies between them and is different from them (a property of ratios).

4.1.2. The determinants $bc - ad$, $m_1b - m_2a$, $m_2c - m_1d$ of a/b, m_1/m_2, c/d (taken two by two) are equal. Conversely, if the determinants of the above type are equal for three ratios, then each one is the median of the other two.

4.1.3. If $bc - ad = 1$, then the median of a/b and c/d is in lowest terms.

4.1.4. If m_1/m_2 is the median of a/b and c/d, then m_2/m_1 is the median of b/a and d/c.

For the construction of the median series, we start with the extreme irreducible fractions 0/1 and 1/0. We denote $M_0 = (0/1, 1/0)$. Any M_{i+1}, $i = 0, 1, 2, \ldots$ is obtained from M_i by itroducing between every two successive terms of M_i their median. Thus we get the median series mentioned in (2.4). M_i is called the median series of i-th order. The following are some of the basic properties of the median series:

4.2.1. Every term in each of the median series is in lowest terms and the terms in a median series are in natural order from left to right and are all distinct. Further any two successive terms in a median series have determinant 1.

4.2.2. Every term of M_i not in M_{i-1} is the median of the two adjacent terms in M_{i-1}. These terms are irreducible. Every term of M_i which occurs also in M_{i-1} is the median of the two adjacent terms in M_i. These terms are however necessarily reducible.

4.2.3. The median series M_i contains $2^i + 1$ terms. Hence the even (odd) terms as counted from the left are also the even (odd) terms as counted from the right. The terms in M_{i+1} that are not in M_i are the even terms and these continue as odd terms in succeeding series.

4.2.4. The r-th term from the left in M_i is the reciprocal of the r-th term from the right. So the middle term is its own reciprocal and so is 1. (It can be seen that the median series of i-th order is got by adding to the Farey series of i-th order, its reflection about 1.)

4.2.5. The middle term of the left half of M_i is $1/2$. The r-th terms to the right and the left of $1/2$ add up to 1.

4.2.6. The r-th term from the left (right) in M_i occurs as the $(2r-1)$-th term from the left (right) in M_{i+1}; hence as $(4r-3)$-th term in M_{i+2} and so in general as $\{2^k(r-1)+1\}$-th term in M_{i+k}.

4.2.7. So if 2^c is the highest power of 2 dividing $r-1$, then r-th term from right (left) of M_i occurs in M_{i-c} as the 2α-th term from the right (left) where

$$\alpha = \frac{r-1}{2^{c+1}} + \tfrac{1}{2}.$$

Being an even term, this term occurs for the first time in M_{i-c}.

§5. The Median Series, (Vahlen's) Approximations and the Enumeration of Positive Rational Numbers

The following is an interpretation based on the idea of approximations to a rational number in terms of the partial quotients $a_0, a_1, a_2, \ldots, a_n$ of the CF expansion of the rational number and this brings out the relation between the approximations and the median series and also the fact that the rational number ρ occurs for the first time (and so as an even term) in $M_{\sigma(\rho)}$.

It is clear that M_0 has no term betewen ρ and $1/0$. It can be seen that the largest value of i such that there is no term between ρ and $1/0$ in M_i is a_0. The penultimate elements $1, 2, 3, \ldots, a_0$ in $M_1, M_2, \ldots, M_{a_0}$ respectively, may therefore be called the first a_0 median approximations to ρ.*

Again the largest value of i such that in M_{a_0+i} there is no term between ρ and $a_0/1$ is evidently a_1. The numbers $a_0 + 1/1, a_0 + 1/2, \ldots, a_0 + 1/a_1$ of $M_{a_0+1}, M_{a_0+2}, \ldots, M_{a_0+a_1}$ respectively, in the interval $(\rho, 1/0)$ give the second set of median approximations to ρ.† Proceeding thus we have

5.1. a_i is the maximum value of t such that there is no term in $M_{a_0+a_1+a_2+\cdots+a_{i-1}+t}$ between ρ and $a_0 + 1/a_1 + 1/a_2 + \ldots + 1/a_{i-1}$ $(i = 2, 3, \ldots, n)$.

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* The successive terms in M_i between which ρ lies are $(i/1, 1/0)$, $i = 1, 2, 3, \ldots, a_0$.

† The successive terms in M_{a_0+i} between which ρ lies are $(a_0/1, a_0 + 1/i)$, $i = 1, 2, 3, \ldots, a_1$.

5.2. The ith set of approximations to ρ are: $a_0 + 1/a_1 + 1/a_2 + \ldots + 1/a_{i-2} + 1/t$ $(t = 1, 2, \ldots, a_{i-1};\ i = 2, 3, \ldots, n+1)$.

5.3. Thus the total number of approximations to ρ is $a_0 + a_1 + \ldots + a_n = \sigma(\rho)$. This shows that ρ occurs for the first time in $M_{\sigma(\rho)}$. It is to be noted that all the convergents of the CF occur among these approximations.

We now proceed to find the exact order in which the convergents a_0, $a_0 + 1/a_1$, $a_0 + 1/a_1 + 1/a_2, \ldots$ occur in the respective median series M_{a_0}, $M_{a_0+a_1}$, ... From the above reasoning relating to the approximations it is clear that

5.4. a_0 and $1/0$ are consecutive in M_{a_0} and ρ lies between them;

5.5. a_0 and $a_0 + 1/a_1$ are consecutive in $M_{a_0+a_1}$ and ρ lies between them; and so on. We note that a_0 occurs in M_{a_0} as the 2^{a_0}-th term and hence occurs in $M_{a_0+a_1}$ as $\{2^{a_1}(2^{a_0} - 1) + 1\}$-th term. Since $a_0 + 1/a_1$ is the term next to a_0 in $M_{a_0+a_1}$ its order is $2^{a_1}(2^{a_0} - 1) + 2$. Hence $a_0 + 1/a_1$ occurs in $M_{a_0+a_1+a_2}$ as the $\{2^{a_2}(2^{a_1+a_0} - 2^{a_1} + 1) + 1\}$-th term. Since $a_0 + 1/a_1 + 1/a_2$ is the term preceding $a_0 + 1/a_1$ in $M_{a_0+a_1+a_2}$ its order is $2^{a_0+a_1a_2} - 2^{a_1+a_2} + 2^{a_2}$. Hence in general

5.6. the i-th convergent $a_0 + 1/a_1 + 1/a_2 + \ldots + 1/a$ occurs in $M_{a_0+a_1+\ldots+a_i}$ as the p-th term where $p = 2^{a_0+a_1+\ldots+a_i} - 2^{a_1+\ldots+a_i} + \ldots + (-1)^i 2^{a_i} + \{1 + (-1)^{i+1}\}$.

Proof.—Let this be true for the i-th convergent. We shall prove that this is then true when i is replaced by $i+1$. The term $(-1)^{i+1}$ indicates that if i is old, the order of $(i+1)$-th convergent in $M_{a_0+\ldots+a_{i+1}}$ is one more and if i is even one less, than the order in $M_{a_0+\ldots a_{i+1}}$ of the i-th convergent. From (5.6) and (4.2.6) the i-th convergent has in $M_{a_0+\ldots+a_{i+1}}$, the order

$$2^{a_{i+1}}(p-1) + 1 = 2^{a_0+\ldots+a_{i+1}} - \ldots + (-1)^{i+1} 2^{a_{i+1}} + 1.$$

Hence the $(i+1)$-th convergent has in $M_{a_0+\ldots+a_{i+1}}$ the order equal to

$$2^{a_0+\ldots+a_{i+1}} - \ldots + (-1)^{i+1} 2^{a_{i+1}} + \{1 + (-1)^{i+2}\},$$

which is the same as (5.6) with $(i+1)$ instead of i. Since the result has been verified for $i = 1, 2$ it holds generally.

The above is also true for the n-th convergent, that is ρ. For the sake of convenience let us take n to be even so that the CF has an odd number of terms. We then have the

THEOREM 1. *A rational number ρ occurs for the first time as* q-*th term in $M_{\sigma(\rho)}$; if ρ has partial quotients* $a_0, a_1, \ldots, a_n$ (n *even*) *then,*

$$q = 2^{a_0+\cdots+a_n} - 2^{a_1+\cdots+a_n} + \ldots + 2^{a_n}$$

$$\rho = a_0 + \frac{1}{a_1} + \frac{1}{a_2} + \ldots + \frac{1}{a_n}.$$

It can be seen that since $a_n > 0$, q is even as ought to be the case since ρ occurs in $M_{\sigma(\rho)}$ for the first time.

COROLLARY.—The number ρ occurs as the $2r$-th term of $M_{\sigma(\rho)}$ where

$$\sigma = \sigma(\rho) = a_0 + a_1 + \ldots + a_n \qquad (n \text{ even})$$

$$r = 2^{\sigma-1} - 2^{\sigma-1-a_0} + \ldots + 2^{a_n-1}.$$

Note.—If $\rho < 1$, then $a_0 = 0$ and in this case the first two terms of r cancel each other.

From the corollary we see that we can associate with the partial quotients of ρ, the integer $r = 2^{\sigma-1} - 2^{\sigma-1-a_0} + \ldots + 2^{a_n-1}$, $\sigma = \sigma(\rho)$ and then we are in a position to say that ρ occurs as the $2r$-th term in $M_{\sigma(\rho)}$. Conversely if we pick out any term in M_i which occurs for the first time, its order is an even number $2r$ and we may show as follows that any such r can be represented as an alternating binary scale representation with odd number of terms starting with $2^{\sigma-1}$.

For, we know that any integer r can be uniquely expressed as an alternating binary scale representation with odd number of terms in the form

$$r = 2^{a_0} - 2^{a_1} + \ldots + 2^{a_n} \qquad (n \text{ even})$$

$$(a_0 > a_1 > a_2 > \ldots > a_n \geq 0).$$

If $r \geq 2^{i-2}$ (so that $\rho > 1$) its alternating binary scale representation will begin with 2^{i-1} and we can, by the corollary, obtain its partial quotients and in particular the first partial quotient of the corresponding $2r$-th term in M_i will be greater than zero. If $r < 2^{i-2}$ (so that $\rho < 1$), the alternating binary scale representation will begin with 2^m $(m \leq i-2)$; we shall then add to this representation the initial term so that

$$r = 2^{i-1} - 2^{i-1} + 2^m - \ldots.$$

The partial quotients are now given in order $(0, i-1-m, \ldots.)$.

5.7. Thus we are not only able to give the precise order $2r$ of the number ρ and the median series M_σ in which it occurs for the first time but

conversely, given any term, say $2r$-th in an arbitrary M_i, we are able to obtain its partial quotients.

Consequently, the corollary establishes a $(1-1)$ correspondence between a given rational number $\rho > 1$ and an integer r in the form of an alternating binary scale representation with odd number of terms, making it possible to enumerate the rational numbers greater than 1.

We next deduce from the corollary, the following theorem which shall be used in the next section.

THEOREM 2. *The sequence of numbers which are the R-th terms from the right in all the median series, form an increasing arithmetic progression with common difference* 1.

Proof

Case 1.—Let R be an even number $2r$. Let ρ be the $2r$-th term from the right in M_i and let it have the partial quotients $a_0, a_1, \ldots, a_n$ (n even). Since $2r$-th term from the right is the $(2^i - 2r + 2)$-th term from the left, we have by Theorem 1, $2(2^{i-1} - r + 1) = 2^i - 2^{i-a_0} + \ldots + 2^{a_n}$ (n even) so that

$$r = 2^{i-1-a_0} - 2^{i-1-a_0-a_1} + \ldots + - 2^{a_n-1} + 1. \tag{5.8}$$

This is therefore the unique alternating binary scale representation for r.

If ρ' be the $2r$-th term from the right in M_{i+k} similarly we have,

$$r = 2^{i+k-1-b_0} - 2^{i+k-1-b_0-b_1} + \ldots - 2^{b_m-1} + 1$$

where $b_0, b_1, \ldots, b_m$ are the partial quotients in the CF expansion of ρ'. Comparing this with (5.8) we have

$$b_0 = a_0 + k; \quad b_i = a_i \,(i > 0); \quad m = n.$$

Thus the terms in M_i and M_{i+k} differ only by k, the difference in the orders of the median series.

Case 2.—Let now R be an odd number $= 2^c j + 1$ (j odd). Then by (4.2.7) it follows that R-th term of M_i occurs as $(j+1)$-th term from the right in M_{i-c} and this is even. Similarly R-th term from the right in M_{i+k} occurs as $(j+1)$-th term from the right in M_{i+k-c}. Since $j+1$ is even, the arguments of case (i) hold here and we have the theorem.

From (4.2.4) we now have

5.9. If the R-th term from the left of M_i is a/b, then the R-th term from the left of M_{i+k} is $(a/ka + b)$.

5.10. Hence, the numerators of the R-th terms from the left in M_i, M_{i+1}, ..., ($R \leq 2^{i+1}$) are the same; that is, the numerator is independent of i. Also, the denominators form an arithmetic progression with common difference equal to the corresponding numerator.

§6. THE RELATION BETWEEN THE TERMS OF THE MEDIAN SERIES AND THE τ-FUNCTION

The corollary under Theorem 1 and (5.7) show that the rational numbers are completely enumerated by the sequence of the median series. If any rational number ρ occurs for the first time in M_σ as $2r$-th term, then we call σ, r as the median co-ordinates of ρ. From what has preceded, the partial quotients of ρ can be found by the expression of r in the alternating binary scale. ρ itself can be expressed by Gaussian brackets in terms of the partial quotients.

But we can adopt a short method by expressing the numerator and the denominator of ρ directly as a function of the median co-ordinates. We may define the numerator of the $2r$-th term from the left in M_i to be $\mu(r, i)$. But from (5.10) it follows that $\mu(r, i)$ is independent of i; that is, $\mu(r, i) = \mu(r)$ say. This is in fact the τ-function of Hermes defined in Section 2. The relation between these two functions is given by $\mu(r) = \tau_r$. Also the denominator of the $2r$-th term in M_i is the numerator of its reciprocal, that is, the $(2^i - 2r - + 2)$-th term. Therefore the denominator of the $2r$-th term is

$$\mu(2^{i-1} - r + 1) = \tau_{(2^{i-1}-r+1)}$$

Thus

$$2r\text{-th term of } M_i = \frac{\tau_r}{\tau_{(2^{i-1}-r+1)}} \quad (r \leq 2^{i-1}), \tag{6.1}$$

and this is in lowest terms.

We now proceed to show a method of calculating τ_r.

We have seen that given a positive integer r which has the unique alternating binary scale representation

$$r = 2^{i-1} - 2^{i-1-a_0} + 2^{i-1-a_0-a_1} - \ldots. + 2^{a_n-1} \ (n \text{ even})$$
$$(a_0 \geq 0, a_n \geq 1),$$

it follows from (2.3.1) and (2.3.2) that

$$\begin{aligned} \tau_r &= [a_n, a_{n-1}, \ldots., a_0] \\ &= [a_0, a_1, \ldots., a_n] \text{ by (3.6)} \\ &= [a_2, a_3, \ldots., a_n] \text{ if } a_0 = 0. \end{aligned}$$

From the alternating binary scale representations of the integers 1, 2, 3, 4, 5, *viz.*,

$$1 = 2^0;\ 2 = 2^1;\ 3 = 2^2 - 2^1 + 2^0;\ 4 = 2^2;\ 5 = 2^3 - 2^2 + 2^0,$$

we get

$$\tau_1 = 1,\ \tau_2 = 2,\ \tau_3 = 3,\ \tau_4 = 3,\ \tau_5 = 4.$$

The recurrence relation for τ_n can be obtained from (5.9). For, from (6.1)

$2r$-th term from the left in

$$M_i = \frac{\tau_r}{\tau_{(2^{i-1}-r+1)}} \quad (r \leq 2^{i-1})$$

Hence

$2r$-th term in

$$M_{i+1} = \frac{\tau_r}{\tau_{(2^i-r+1)}}$$

$$= \frac{\tau_r}{\tau_r + \tau_{(2^{i-1}-r+1)}} \qquad \text{(by 5 9)}$$

As these have been remarked to be in lowest terms we get,

$$\tau_{(2^i-r+1)} = \tau_r + \tau_{(2^{i-1}-r+1)} \qquad (r \leq 2^{i-1})$$

Replacing i by $(i+1)$ and the r by $(2^i - a + 1)$ we get

$$\tau_{(2^i+a)} = \tau_a + \tau_{(2^i-a+1)} \qquad (a \leq 2^i) \qquad (6.2)$$

This is precisely the recurrence relation of Hermes[1] (p. 372).

We can now calculate any term (say k-th from the left) of any M_i. Let the term be denoted by $T(k, i)$.

Case 1.—Let k be even $= 2r$.

Then

$$T(k, i) = \frac{\tau_r}{\tau_{(2^{i-1}-r+1)}}$$

by (6.1)

$$= \frac{\tau_{k/2}}{\tau_{\frac{1}{2}(2^i-k+2)}}$$

Case 2.—When k is odd, $k+1$ and $k-1$ are both even. Since k-th term of M_i is the median of the adjacent terms, we have

$$T(k, i) = \frac{\tau_{\frac{1}{2}(k-1)} + \tau_{\frac{1}{2}(k+1)}}{\tau_{\frac{1}{2}(2^i-k+3)} + \tau_{\frac{1}{2}(2^i-k+1)}} \tag{6.3}$$

Or alternately, when k is odd, write $k = 2^c j + 1$ (j odd). Then this term occurs for the first time as $(j+1)$-th term in M_{i-c}, *i.e.*, as the $(j+1)/2$-th even term.

Hence $T(k, i) = T(j+1, i-c)$. Hence by case (1) we have

$$T(k, i) = \frac{\tau_{(j+1)/2}}{\tau_{\frac{1}{2}(2^{i-c}-j+1)}} \qquad \text{where } k = 2^c j + 1. \tag{6.4}$$

It can be verified that (6.3) and (6.4) are the same, using τ-function properties.

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THERMO-ELASTIC BEHAVIOUR OF CUBIC CRYSTALS

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1. Introduction

Experimental studies of the elastic properties of single crystals are of great significance from the standpoint of solid state physics. Such studies, when extended to higher temperatures, are likely to throw light on the nature of interatomic and interionic forces in crystals. Hitherto, though it has been possible to obtain data for quite a large number of single crystals at room temperatures, extensive work on their temperature variation was not done. Hence it was thought worthwhile to study the temperature dependence of the elastic moduli of some cubic crystals.

Eight cubic crystals, elastic constants of which have already been studied at room temperature by Bhagavantam and his co-workers, have been chosen for the investigation in the temperature range 30–300° C. Some of the more important results have been published in a recent review article in these *Proceedings* (Bhagavantam, 1955).

2. Experimental Details

The composite piezoelectric oscillator method, originally developed by Balamuth (1934) and Rose (1936) has been employed in the present investigation. In this technique, the specimen crystal in the form of a bar is cemented, with a suitable adhesive, to a quartz rod of identical cross-section. The fundamental resonant frequencies of the quartz and the composite system are determined separately and the natural frequency of the specimen is computed therefrom. The method of finding out the frequencies makes use of the fact that at resonance the impedance of the system undergoes a marked reduction. With a knowledge of the resonant frequency, length and density of the specimen, one elastic constant or one combination of elastic constants, can be calculated.

Quartz rods of 0·30 cm. square cross-section are used to excite the longitudinal mode. Torsional vibrations are excited by a Y-cut quartz rod of circular cross-section and 0·30 to 0·40 cm. in diameter, with the electrode

arrangement as suggested by Giebe and Scheibe (1928). The composite oscillator with its holder is placed at the centre of an electric furnace and the temperature is controlled by varying the heating current.

The lengths of the specimens are measured at room temperature on comparator. The densities are determined by the hydrostatic method. Densities and lengths at higher temperatures are evaluated using the data on thermal expansion, available in the literature.

Young's modulus, Y, and the rigidity modulus, n, along (100), (110) and (111) directions are directly determined and the elastic moduli are evaluated using the formulæ:—

$$1/Y_{(100)} = s_{11}; \quad 1/n_{(100)} = s_{44}$$

$$1/Y_{(110)} = \tfrac{1}{2}(s_{11} + s_{12} + \tfrac{1}{2}s_{44}); \quad 1/n_{(110)} = s_{11} - s_{12} + \tfrac{1}{2}s_{44}$$

$$1/n_{(111)} = 4/3\,(s_{11} - s_{12}) + \tfrac{1}{3}s_{44}.$$

The elastic constants, c's are computed using the well-known formulæ.

The estimated uncertainty in s_{11} and s_{44} is one per cent. A small percentage error in measurement is very greatly magnified in the calculation of the difference quantity s_{12}. The uncertainty in s_{12} varies from 2 to 3 per cent. over the temperature range. With this method, changes in moduli can be more accurately measured than their absolute values.

3. Results and Discussion

(*a*) *Alkali halides.*—Among the cubic crystals, the alkali halides constitute an important group whose physical properties have been investigated extensively. Direct theoretical evaluation of the elastic constants has also met with some success in this case.

The effect of temperature on the elastic moduli of KCl and KBr has been studied up to room temperature by Durand (1936) and Galt (1948) respectively. In the present investigation these studies have been extended to 300° C. and LiF, which belongs to the same type of structure, has been freshly studied.

Ammonium chloride is an interesting case among alkali halides. It has a body-centred CsCl structure at room temperature and changes over to the NaCl type at higher temperatures. Thermo-elastic behaviour of ammonium chloride is studied with a view to compare it with that of the NaCl type halides.

In Table I, two constants characterising the thermal behaviour of crystals in longitudinal and torsional modes are given. The constant represents the

variation of the elastic modulus with temperature expressed as a fraction of its value at room temperature.

The data on NaCl (Subrahmanyam, 1954) are also included to facilitate a comparison of alkali halides. The s's and the c's are respectively expressed in units of 10^{-13} cm.^{2}/dyne and 10^{11} dynes/cm.^{2}

TABLE I

Thermo-elastic constants of alkali halides

Substance	$\frac{1}{s_{11}}\frac{d(s_{11})}{dt}\times 10^5$	$\frac{1}{s_{44}}\frac{d(s_{44})}{dt}\times 10^5$
NaCl ..	155	35
KCl ..	93	30
KBr ..	113	22
LiF ..	92	27
NH_4Cl ..	40	172

Experimental results reveal the following points regarding the thermo-elastic behaviour of alkali halides.

1. Rate of variation of s_{11} with temperature is greater than that of s_{44} in the alkali halides of NaCl type.

2. Contrary is the case with ammonium chloride as the variation of s_{44} is greater than that of s_{11} in this case. Ammonium chloride belongs to the CsCl type structure.

3. s_{12} decreases with increasing temperature in the NaCl type halides. It increases in the case of ammonium chloride.

4. Elastic constants c_{11}, c_{12} and c_{44} all decrease with increasing temperature in all cases.

5. In the case of thermo-elastic constants for the shear mode, there is a striking difference between the alkali halides of NaCl and CsCl types. The value of the constant for NaCl type halides is about 30 while its value in the case of ammonium chloride is 172. In other words, the rate at which s_{44} increases or c_{44} decreases with temperature in the case of ammonium chloride s very much greater than that in the case of NaCl type halides. This can be

explained as due to the low melting point of ammonium chloride and correspondingly high values for the NaCl type halides. As the melting point is approached the lattice loses its resistance to shearing more rapidly than at temperatures far removed from the melting point.

(*b*) *Other crystals.*—The results of measurements made on Iron pyrites, Fluorite and Galena are presented in Table II.

TABLE II

Substance	Temp. range °C.	$\frac{1}{s_{11}}\frac{d(s_{11})}{dt}\times 10^5$	$\frac{1}{s_{44}}\frac{d(s_{44})}{dt}\times 10^5$	Variation of s_{12}
FeS_2 ..	30–300	17	23	+0·2 to +0·35
CaF_2 ..	30–300	35	39	−1·7 to −1·80
PbS ..	30–200	45	65	−2·0 to −2·30

Iron pyrites crystallises in the cubic system and belongs to the T_h class. Its elastic constants have been determined by Voigt (1928) using static methods. He reported a positive value for s_{12}. Later on, dynamic methods have been applied to study its elastic behaviour by Bhagavantam and Bhimasenachar (1944) and Doraiswami (1947) amongst others. In this work, crystal rods are cut from a well formed two-inch cube. The results clearly show a positive value for s_{12}. This positive sign persists throughout the temperature range (30–300° C.). Pyrites is unique among crystals to exhibit such a peculiar elastic behaviour. s_{11} and s_{44} vary almost linearly with temperature and s_{12} practically remains constant in all the three cases.

The results for magnetite are presented in Fig. 1. Magnetite crystallises in the holohedral class of the cubic system. It possesses a curie point at 575° C. and the symmetry of the crystal changes from cubic to orthorhombic at 119° C. Elastic constants of magnetite vary with temperature in an unusual manner. Elastic constants of solids generally decrease with increasing temperature provided there is no change of state. However, as can be seen from Fig. 1, Young's modulus along (100) direction decreases as usual while the rigidity in the same direction increases. The increase is definite, though small. Along (111) direction the behaviour is exaclty the reverse. Rigidity decreases with increasing temperature while the Young's modulus increases.

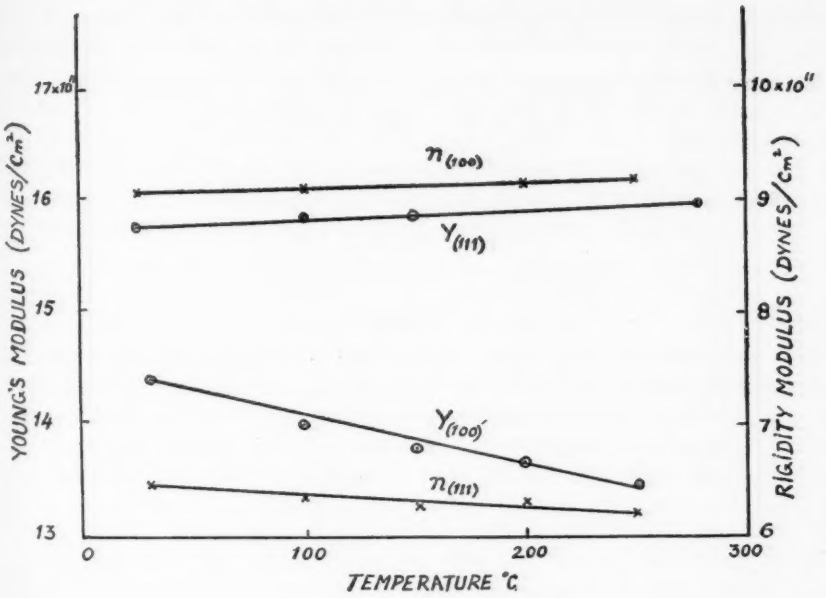

FIG. 1. Magnetite.

4. SUMMARY

The composite piezoelectric oscillator method has been employed to study the temperature dependence of the elastic moduli of single crystals of KCl, KBr, LiF, NH_4Cl, FeS_2, Fe_2O_3, CaF_2 and PbS in the temperature range 30–300° C.

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ZENITH ANGLE RESPONSE OF A VERTICAL MESON TELESCOPE

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Abstract

Expressions have been obtained for the Geometrical Sensitivity as a function of the zenith angle of a cosmic ray telescope comprising of counter trays of rectangular dimensions. The Radiation Sensitivity and Cumulative Sensitivity have also been calculated, assuming a zenith angle attenuation of the form $I_\theta = I_\theta.\cos^2\theta$ for cosmic ray intensity.

I. Introduction

Measurements of cosmic ray intensity in the vertical direction are mostly carried out by Geiger counter telescopes which comprise of a series of counter trays of rectangular dimensions situated one above the other. All counters in the same tray are connected in parallel and the pulses from the various trays are fed to a coincidence unit which gives a sizable pulse in the output only if pulses are fed to all its inputs within a small time interval, termed as the "resolving time" of the coincidence unit. The coincidence output rate corresponds to single charged particles passing through all the counter trays except for (1) a contribution due to showers where different trays could be triggered by different particles all belonging to the same shower and hence arriving almost simultaneously and (2) a contribution due to chance coincidences where different trays could be triggered by different particles apparently unrelated to each other. For coincidence units with resolving times of the order of a few microseconds as is usually the case and for more than two counter trays in coincidence, the contribution of chance coincidences is negligible. The contribution of side showers depends on the material in the near environment of the telescope and on the separation of the trays. Under optimum conditions this does not exceed about 7% for triple coincidence telescopes, as investigated by Greisen and Nereson.[1] Thus the vast majority of counts registered by such a counter telescope are due to cosmic radiation incident in the cone within which a single particle can cross all the trays.

A vertical meson telescope is characterised by (*a*) its dimensions which may be given as length, breadth and separation of the end trays or, alternatively, the semi-angles subtended by the telescope in two mutually perpendicular planes and the separation of the end trays, (*b*) the amount of absorber used in between the top and bottom trays. Once these characteristics are known it is possible to evaluate the expected counting rate of the telescope from known values of the vertical flux of cosmic ray intensity at the place of observation and the zenith angle dependence of the same.

A vertical meson telescope offers a maximum sensitive area for particles coming in the vertical direction. A simple geometrical consideration shows, however, that the solid angle available for particles coming in inclined directions is greater than the one available for those coming in a vertical direction. Taking into account both these factors one can calculate the Geometrical Sensitivity G.S. (θ) of any telescope arrangement for different values of the inclination θ which the incoming cosmic ray trajectories make with the vertical. Parsons[2] has obtained an expression for the same in case of a meson telescope of cubical symmetry which is recommended as standard equipment for the current International Geophysical Year. His method can, however, be extended to counter telescopes of any dimensions. We have attempted here to get a general expression for telescopes of any given dimensions.

II. Geometrical Sensitivity of A Vertical Meson Telescope

Consider a geometrical arrangement (Fig. 1) in which the top and bottom trays are represented by ABCD and A′B′C′D′ respectively. Let the length $AB = A'B' = CD = C'D' = l$ and breadth $BC = AD = B'C' = A'D' = d$. The separation between the two trays is $AA' = BB' = CC' = DD' = a$.

If the ratios l/a and d/a are denoted by Δ and δ respectively, the semi-angles of the telescope in the two vertical planes one along the length and the other perpendicular to it are $\tan^{-1}(\Delta)$ and $\tan^{-1}(\delta)$ respectively. The most inclined direction the telescope can record has a zenith angle $\theta = \tan^{-1} \sqrt{l^2 + d^2}/a = \tan^{-1} \sqrt{\Delta^2 + \delta^2}$ and corresponds to rays parallel to the diagonals AC′, BD′, CA′ or DB′.

Consider cosmic rays incident along a zenith angle θ and an azimuth α, where $\alpha = 0$ for a direction parallel to the breadth 'd' of the counter trays. The beam will then be incident on the rectangular area OXD′Y of the lower tray where

$$OX = (l - a \cdot \tan\theta \cdot \sin\alpha) \text{ and}$$
$$OY = (d - a \cdot \tan\theta \cdot \cos\alpha) \qquad (1)$$

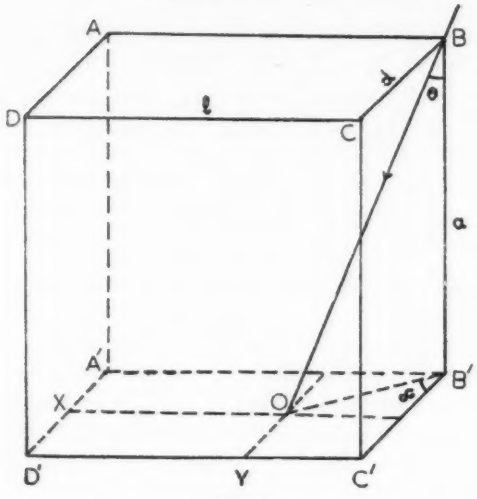

FIG. 1

The effective cross-sectional area of the telescope normal to the beam would be

$$A = \cos\theta \cdot (l - a \cdot \tan\theta \cdot \sin\alpha) \cdot (d - a \cdot \tan\theta \cdot \cos\alpha). \qquad (2)$$

Consider the shaded area (Fig. 2) normal to the direction of incidence of a beam which has a zenith angle ranging from θ to $(\theta + d\theta)$ and azimuth

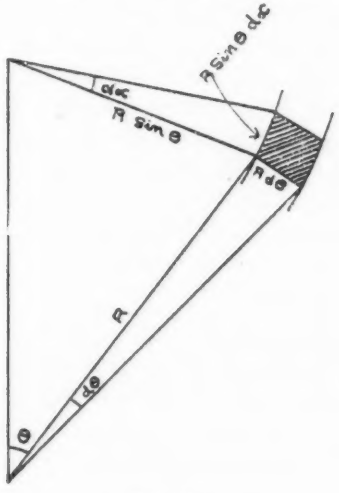

FIG. 2

from α to $(\alpha + d\alpha)$. The solid angle subtended by this beam at the centre of the telescope is given by

$$dw = \frac{(R.\sin\theta.d\alpha).R d\theta}{R^2}$$

$$= \sin\theta.d\theta.d\alpha \qquad (3)$$

The relative Geometrical Sensitivity of the telescope for directions confined to zenith angles between θ and $(\theta + d\theta)$ and azimuth between α and $(\alpha + d\alpha)$ is given by

$$\text{G.S.}(\theta).d\theta.d\alpha = A.\sin\theta.d\theta.d\alpha \qquad (4)$$

The total relative Geometrical Sensitivity of the telescope corresponding to a zenith angle θ is

$$\text{G.S.}(\theta) = \int_{\alpha_1}^{\alpha_2} A.\sin\theta.d\alpha$$

$$= \sin\theta.\cos\theta\,[l\,d.(\alpha_2 - \alpha_1) - a.\tan\theta.l.(\sin\alpha_2 - \sin\alpha_1) + a.\tan\theta.d.(\cos\alpha_2 - \cos\alpha_1) - (a^2/4).\tan^2\theta.(\cos 2\alpha_2 - \cos 2\alpha_1) \qquad (5)$$

Putting $(d/a) = \delta$ and $(l/a) = \Delta$,

$$\frac{\text{G.S.}(\theta)}{a^2} = \sin\theta.\cos\theta\,[\Delta.\delta.(\alpha_2 - \alpha_1) - \Delta.\tan\theta.(\sin\alpha_2 - \sin\alpha_1) + \delta.\tan\theta.(\cos\alpha_2 - \cos\alpha_1) - (\tan^2\theta/4).(\cos 2\alpha_2 - \cos 2\alpha_1)] \qquad (6)$$

where α_1 to α_2 is the range of azimuth for which the effective cross-sectional area A has positive values.

Assuming that the breadth 'd' is less than the length 'l', the zenith angle θ can be grouped into three ranges for each of which a set of values of α_1 and α_2 would be effective.

Case 1.—$0 < \theta \leqslant \tan^{-1}(\delta)$. For this range, the azimuth values range from 0 to 2π. Since, however, all the quadrants are symmetrical, it is sufficient to integrate from 0 to $\pi/2$. Thus $\alpha_1 = 0$ and $\alpha_2 = \pi/2$.

Case 2.—$\tan^{-1}(\delta) < \theta \leqslant \tan^{-1}(\Delta)$. For values of θ in this range (*see* Fig. 3) the particle would miss the telescope for azimuth $\alpha = 0$. The

cross-sectional area A will first become positive for values of azimuth given by

$$\cos \alpha_1 = \frac{d}{D} = \frac{d/a}{D/a} = (d/a).\cot \theta = \delta.\cot \theta$$

Thus the lower limit is $\alpha_1 = \cos^{-1}(\delta.\cot \theta)$. The upper limit for integration is still $\pi/2$ as in case 1.

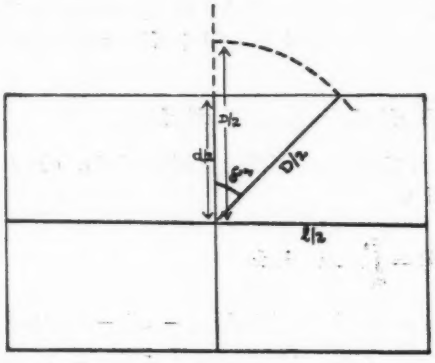

FIG. 3

Case 3.—$\tan^{-1}(\Delta) < \theta \leqslant \tan^{-1}\sqrt{\Delta^2 + \delta^2}$. For this region (*see* Fig. 4) the particles will have a positive cross-sectional area for values of α between α_1 and α_2, where

$$\alpha_1 = \cos^{-1}(\delta.\cot \theta) \text{ and } \alpha_2 = \pi/2 - \cos^{-1}(\Delta.\cot \theta).$$

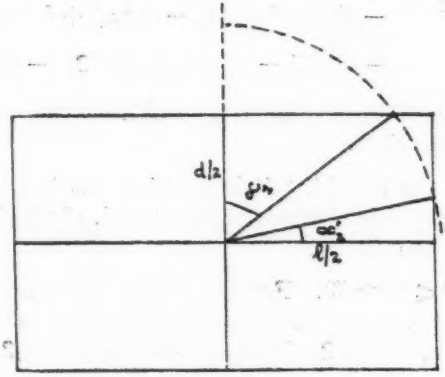

FIG. 4

For isotropic radiation incident upon the telescope, G.S. (θ) is directly proportional to the number of particles coming at a zenith θ. If, however, there is a zenith angle dependence of the cosmic radiation of the form

$$I_\theta = I_0 \cdot \cos^\lambda \theta \tag{7}$$

the Radiation Sensitivity R.S. (θ) is given by

$$\text{R.S.}(\theta) = \cos^\lambda \theta \cdot \text{G.S.}(\theta). \tag{8}$$

III. Results

In Figs. 5, 6 and 7, the relative Geometrical Sensitivity and Radiation Sensitivity for various values of the semi-angles $\tan^{-1}(\delta)$ and $\tan^{-1}(\Delta)$ of a telescope are plotted. The value chosen for λ is 2.

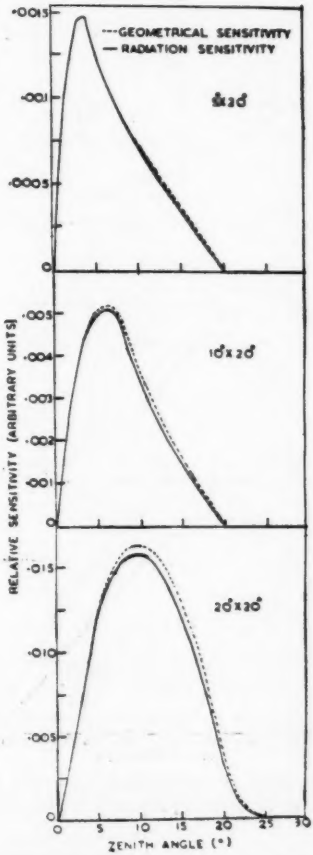

Fig. 5. Zenith angle dependence of Geometrical Sensitivity and Radiation Sensitivity for a telescope having a semi-angle of 20° in one plane and 5°, 10° and 20° in a perpendicular plane.

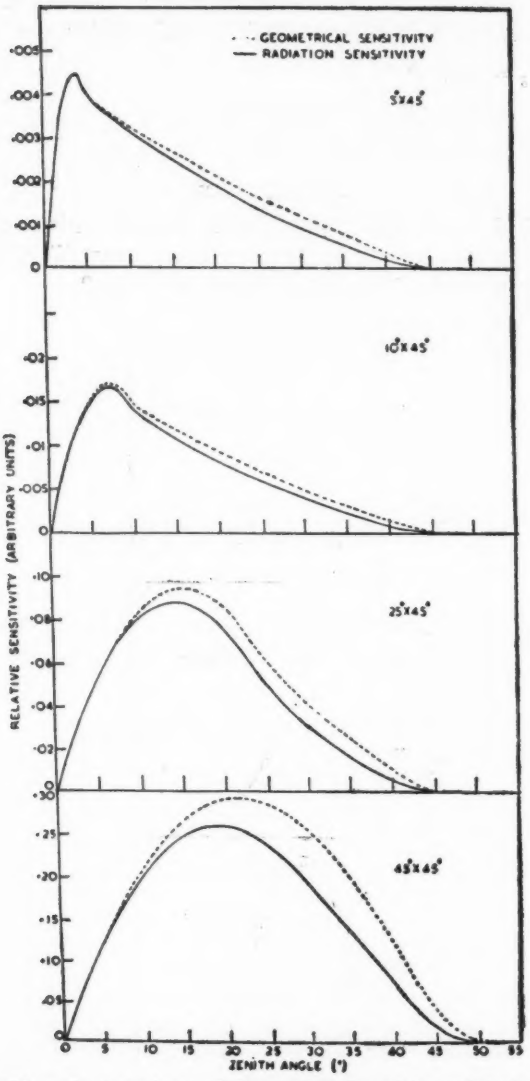

FIG. 6. Zenith angle dependence of Geometrical Sensitivity and Radiation Sensitivity for a telescope having a semi-angle of 45° in one plane and 5°, 10°, 25° and 45° in a perpendicular plane.

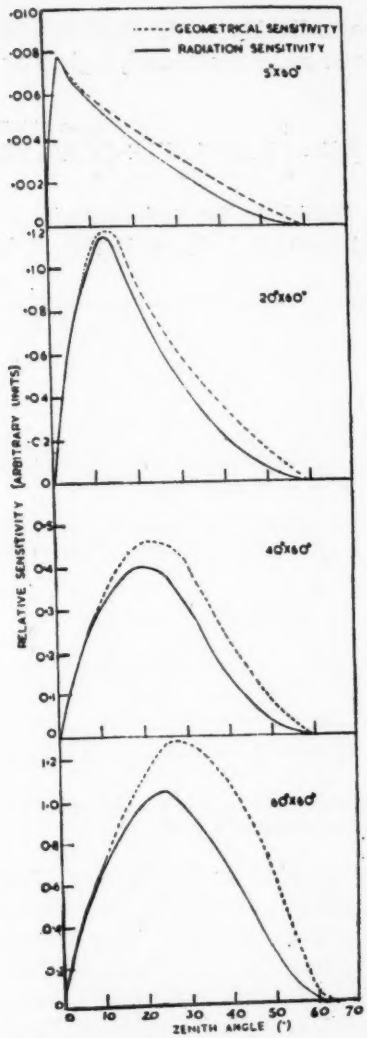

FIG. 7. Zenith angle dependence of Geometrical Sensitivity and Radiation Sensitivity for a telescope having a semi-angle of 60° in one plane and 5°, 20°, 40° and 60° in a perpendicular plane.

The total counting rate of a telescope is given by

$$N = 4I_0 \cdot \int_{\theta}^{\tan^{-1}\sqrt{\Delta^2+\delta^2}} \text{R.S.}(\theta) \cdot d\theta \qquad (9)$$

The percentage contribution to the total rate of particles confined to the zenith angles between 0 and any value θ_0 is given by the Cumulative Sensitivity C.S. as

$$\text{C.S.} = [100 \cdot \int_0^{\theta_0} \text{R.S.}\,(\theta).d\theta] \div [\int_0^{\tan^{-1}\sqrt{\Delta^2+\delta^2}} \text{R.S.}\,(\theta).d\theta] \qquad (10)$$

The Cumulative Sensitivity for various zenith angles and for various values of $\tan^{-1}(\delta)$ and $\tan^{-1}(\Delta)$ is shown in Figs. 8, 9 and 10.

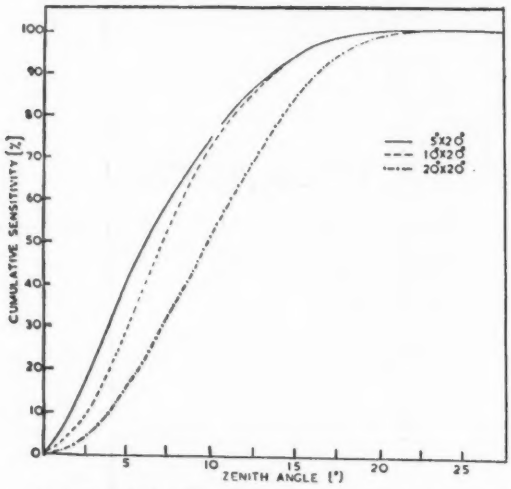

FIG. 8. Percentage Cumulative Sensitivity of a telescope having a semi-angle of 20° in one plane and 5°, 10° and 20° in a perpendicular plane.

A striking feature revealed by the plots of Cumulative Sensitivity is that the bulk of the radiation is confined to comparatively small zenith angles in spite of large opening of the telescope. Thus, for a telescope having semi-angles as large as 60° in both the East-West and North-South planes, about 70% of the radiation is confined to zenith angles less than about 35°. The bias towards smaller zenith angles is increased still further if one of the semi-angles of the telescope is small. For example, a telescope having semi-angles 20° and 60°, counts 70% of its counting rate within zenith angles of 0 to 25°.

In designing a telescope for a particular investigation, the research worker is interested in the directional sensitivity of his instrument. The present work enables the investigator to decide the shape of a counter tray which would satisfy requirements of directional sensitivity in the most appropriate

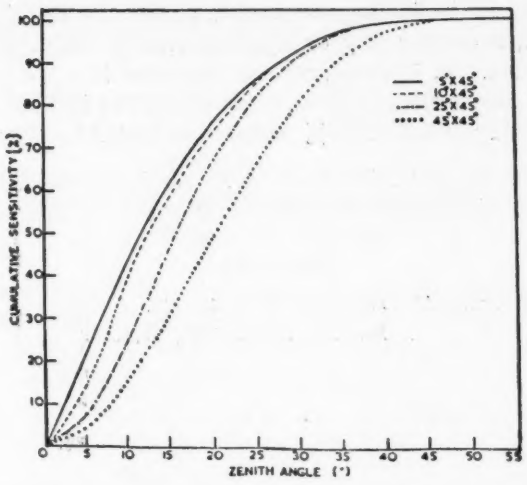

FIG. 9. Percentage Cumulative Sensitivity of a telescope having a semi-angle of 45° in one plane and 5°, 10°, 25° and 45° in a perpendicular plane.

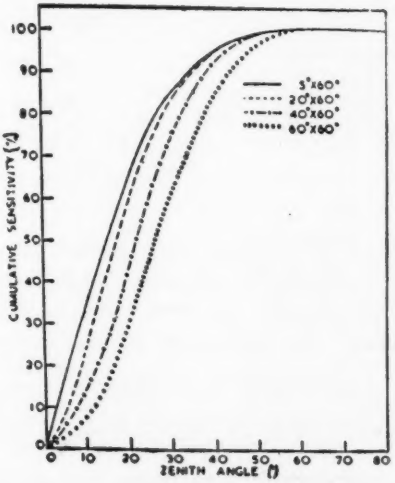

FIG. 10. Percentage Cumulative Sensitivity of a telescope having a semi-angle of 60° in one plane and 5°, 20°, 40° and 60° in a perpendicular plane.

way. If, for example, the requirements specify an 80% response due to particles within 10° inclination with zenith, irrespective of azimuth of direction of arrival, a counter tray of square geometry obviously provides the optimum solution. If, however, we are interested in a narrow angle of 5° in the E.-W. plane, a rectangular tray of dimensions 1 : 4 in the E.-W. and N.-S. planes would still provide an 80% response restricted to 10° with zenith.

The authors are grateful to Prof. V. A. Sarabhai for helpful discussions and to the Atomic Energy Commission of India for financial assistance.

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ALKALOIDS OF *MAHONIA NEPALENSIS* D.C.

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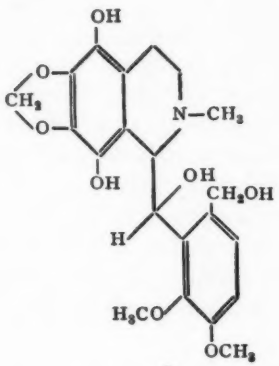
From *Mahonia nepalensis* D.C., Chatterjee[1] reported the isolation of an yellow base umbellatine, $C_{21}H_{21}O_8N$, m.p. 205–07° (decomp.) and a red base neprotine, $C_{19}H_{23}O_6N$. Earlier Chatterjee had reported the isolation of umbellatine from *Berberis umbellata*[2] and *Berberis insignis*.[3] On the basis of degradation work umbellatine was assigned the structure I[4] and neprotine the structure II.[5]



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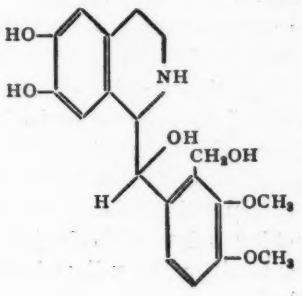

II

Both these structural formulæ have unusual features and a re-examination of the alkaloids of *Mahonia napalensis* appeared desirable. Following the procedure of Chatterjee two bases were isolated by us, a yellow base, m.p. 205–07° (decomp.) and a red base, m.p. 206° (decomp.).

The yellow base was characterised by preparation of a crystalline sulphate and a picrate whose melting points were in good agreement with those of the corresponding derivatives of Chatterjee's umbellatine. Analysis of the yellow base after drying at 110° *in vacuo* gave values in agreement with the molecular formula $C_{20}H_{19}O_5N$, 3 H_2O. Reduction of the 'hydrochloride' of the yellow base in alcohol solution in presence of Adams catalyst yielded

a hydrochloride, m.p. 215–17°, from which a colourless base, m.p. 172°, analysing for the formula $C_{20}H_{21}O_4N$ was obtained. The identity of the last compound with *dl*-tetrahydroberberine was established by mixed melting point determination with an authentic sample. Reduction of the hydrochloride of the yellow base with lithium aluminuim hydride yielded a base, m.p. 164°, identical with dihydroberberine (m.p. and mixed m.p.). The yellow base gave an acetone compound, m.p. 168°, identical with berberine acetone compound (m.p. and mixed m.p.). A sample of berberine regenerated from berberine sulphate (B.D.H.) after one crystallisation from alcohol yielded crystals, m.p. 145° (decomp.). A second crystallisation from alcohol gave crystals, m.p. 205–07°.* The latter gave no depression in melting point with the yellow base from *Mahonia nepalensis*. It is therefore proved that umbellatine is identical with berberine.

It is curious that the m.p. 205–07° has not so far been recorded in literature for berberine. Katti and Shintre[6] isolated from *Coscinium fenestratum* Coleb an alkaloid, m.p. 205°, whose identity was not established. Pillai and Varrier[7] in a reinvestigation of this plant obtained an alkaloid whose identity with berberine was established by conversion to the acetone compound from which the form of berberine, m.p. 145°, was regenerated. It is also strange that melting or decomposition points have not been recorded for many of the salts of berberine. It is true that berberine and its salts undergo considerable colour change before melting, but it was observed in the present work that the hydrochloride, the sulphate and the picrate all *melt* with decomposition after a considerable preliminary darkening of colour. The melting points of berberine and its derivatives and the corresponding compounds from the yellow base of the *Mahonia nepalensis* are recorded in Table I.

Chatterjee has reported that the red base obtained from *Mahonia nepalensis* charred without melting. From the present work it was found that the red base melted at 206–08° (decomp.) and yielded a picrate, m.p. 210-11° (*cf.* Chatterjee 208–10°). The red base analysed for the formula $C_{20}H_{21}O_5N$, $3\,H_2O$. Reduction of the 'hydrochloride' of the red base proceeded with absorption of two moles of hydrogen, yielding a tetrahydro base $C_{20}H_{23}O_4N$, m.p. 206–07°, which after methylation with diazomethane, yielded a compound m.p. 146°, identical with *dl*-tetrahydropalmatine. Ethylation of the

* Prof. K. Venkataraman (private communication) obtained a base, m.p. 205–06°, from *Coscinium fenestratum*, which gave an acetone compound identical with that from berberine. He also noted that berberine from commercial berberine sulphate melted at 145° after one crystallisation and at 205–207° after a second crystallisation from alcohol.

tetrahydrobase with diazoethane yielded an ethyl ether, m.p. 124°. A sample of *l*-corypalmine was ethylated, oxidised with iodine and reduced with zinc and hydrochloric acid to yield *dl*-O-ethyltetrahydrojatrorrhizine, m.p. 124°, identical with the ethyltetrahydroneprotine above. It is thus established that neprotine is identical with the known alkaloid jatrorrhizine. The relevant melting point data is presented in Table II.

TABLE I

	The yellow base (present work) m.p.	Umbellatine (Chatterjee's work) m.p.	Berberine m.p.
Base ..	205–07° (decomp.)	206–07°[8] (decomp.)	145°[9]
Hydrochloride ..	206° (decomp.)	..	205–07° (decomp.)
Sulphate ..	274° (decomp.)	274°[8] (decomp.)	274° (decomp.)
Picrate ..	234° (decomp.)	232°[8] (decomp.)	232° (decomp.)
Acetone compound ..	168°	..	168°[10]
Product from treatment with dimethyl sulphate	284° (decomp.)	265°[8]	284° (decomp.)
Tetrahydrobase ..	171°	213–15°[8]	171°[11]
Dihydro base ..	164°	[8]Charred without melting	164°[12]

TABLE II

	The red base (present work) m.p.	Neprotine (Chatterjee's work) m.p.	Jatrorrhizine m.p.
Base ..	206° (decomp.)	Charring[1] without melting	..
Hydrochloride ..	206–08° (decomp.)	Charrs[1] above 200° without melting	206° (decomp.)
Nitrate ..	225° (decomp.)	..	225°[14] (decomp.)
Picrate ..	210–211° (decomp.)	208–10°[13] (decomp.)	..
Tetrahydrobase ..	206°	..	206°[5]
O-Ethyltetrahydro base	124°	..	120°[15]
O-Methyltetrahydro base	146°	..	146°[16]

EXPERIMENTAL

Plant material was supplied by Messrs. Ghosh and Co., Darjeeling.

Isolation of the alkaloids of Mahonia nepalensis *D.C.*—Air-dried powdered roots and stem bark of the plants (2·5 kg.) were treated with alcohol (5·1). After two days, the yellow solution was drawn off and distilled on a water-bath. The brown residue was treated with water (500 c.c.), filtered, and the filtrate was treated with hydrochloric acid (congo red) and allowed to stand overnight. Crystals of the yellow base hydrochloride separated and were filtered and well washed, until the washings were yellow in colour. The brown filtrate was concentrated on a water-bath to 400 c.c. and filtered twice. On leaving this solution overnight, a second crop of yellow crystals appeared. The solution was decanted carefully into a shallow dish, evaporated partially and was left to crystallise. After two days red granules appeared and the dish was left undisturbed for a week till the quantity of granules stopped increasing. The red granules were filtered, washed and dried. Further spontaneous evaporation of the filtrate gave only a sticky brown mass which could not be crystallised.

Yellow base hydrochloride.—The foregoing yellow hydrochloride was crystallised first from hot water containing a few drops of hydrochloric acid. Recrystallisation from alcohol gave the *hydrochloride* (4·8 g./kg. of plant material) as yellow silky needles, m.p. and mixed m.p. with berberine hydrochloride, 206° (decomp.).

Yellow base.—The purified hydrochloride (4 g.) was dissolved in hot water and a dilute solution of sodium carbonate was added until alkaline, whereupon the yellow colour of the solution changed to dark brown, and on cooling, yellow silky needles of the free alkaloid (3 g.) were obtained. Repeated crystallisation from alcohol gave the *base*, m.p. 205–07° (decomp.). Found: C, 59·0; H, 5·9; N, 3·4. $C_{20}H_{19}O_5N.3\ H_2O$ requires C, 59·0; H, 6·4; N, 3·4%. The melting point was undepressed by admixture with the higher melting form of berberine prepared as below:—

Berberine sulphate (B.D.H.) was suspended in water and basified by adding saturated sodium carbonate solution. The solid was filtered and crystallised once from alcohol when yellow crystals of berberine, m.p. 145° were obtained. A second crystallisation from alcohol changed the m.p. to 205–07°.

The *sulphate* was prepared as usual and crystallised from alcohol had m.p. and mixed m.p. with berberine sulphate (B.D.H.) 274° (decomp.).

Picrate.—The picrate was prepared as usual and was crystallised from alcohol. It had m.p. and mixed m.p. with berberine picrate, 234° (decomp.).

The acetone compound.—The yellow base hydrochloride (0·2 g.) dissolved in water (15 c.c.) was treated with sodium hydroxide solution (10%; 4 c.c.) and heated to 50°. Acetone (10 c.c.) was added and the solution set aside when lemon-yellow needles of the acetone compound separated, which melted at 168°. Mixed with berberine-acetone compound, there was no depression in the melting point.

Treatment of the yellow base with dimethyl sulphate.—An excess of dimethyl sulphate was added drop by drop to a solution of the yellow base (0·1 g.) in 10% potassium hydroxide solution with constant shaking. After half hour, yellow, silky fine needles separated. The shaking and the addition of dimethyl sulphate were continued and the mixture was kept alkaline. After one hour, the crystals were filtered, well washed with water, dried and then recrystallised from alcohol as silky yellow needles, m.p. 284°, undepressed by admixture, with the product, m.p. 284°, obtained from berberine by a similar procedure (Found: C, 55·0; H, 4·2%).

Dihydrobase.—To a suspension of lithium aluminium hydride (0·8 g.) in ether (100 c.c.), the yellow base hydrochloride (0·5 g.) was added during the course of 15 minutes, and the stirring was continued for 12 hours. The complex was decomposed as usual and repeatedly extracted with ether. After the removal of ether, the dihydrobase was obtained as yellow crystals (0·25 g.). After recrystallisation from ether, the *dihydro compound* had m.p. and mixed m.p. with dihydroberberine, 164° (Found: C, 70·8; H, 5·3. $C_{20}H_{19}O_4N$ requires C, 71·2; H, 5·6%).

Tetrahydrobase.—A solution of the yellow base hydrochloride (0·5 g.) in absolute alcohol (40 c.c.) containing platinum oxide (0·2 g.) was hydrogenated at 50 lb./sq. in. After the removal of solvent, the hydrochloride was obtained as a white powder, which crystallised from alcohol, had m.p. 215–17°. The free base was obtained after basification with liquor ammonia. After recrystallisation from alcohol, the *tetrahydro compound* was obtained as white needles, m.p. and mixed m.p. with tetrahydroberberine, 172° (Found: C, 70·6; H, 6·2. $C_{20}H_{21}O_4N$ requires C, 70·8; H, 6·2%).

Oxidation of the yellow base with potassium permanganate.—The base hydrochloride (0·5 g.) was dissolved in warm water (20 c.c.) and treated with potassium carbonate (0·15 g.) and then oxidised by slowly running in a solution of potassium permanganate (2·5 g. in 50 c.c. of water). The decolourisation of the permanganate was very rapid at first and then slowed down

appreciably after 30 c.c. of the solution had been added. The contents were warmed on a water-bath for 3 hours, and left aside overnight. The mixture was filtered and the residual manganese dioxide was extracted twice with hot water and the combined filtrate concentrated to 30 c.c. The solution was acidified with concentrated hydrochloric acid (congo red) and extracted continuously with ether for several hours. After the removal of solvent, the gummy residue left behind was sublimed *in vacuo*. The sublimate was dissolved in ethanol (5 c.c.) and anhydrous ethyl amine (3 c.c.) was added and the solution was evaporated on a water-bath. The residue was heated at 180° for 5 minutes and then sublimed *in vacuo*. The sublimate was crystallised from dilute alcohol to yield N-ethylhemipinimide as white, slender needles, m.p. and mixed m.p. with an authentic specimen, 90°.

The red base hydrochloride.—The red hydrochloride from the extraction of *Mahonia nepalensis* D.C. was crystallised from hot water containing a few drops of hydrochloric acid; the crystals were filtered and recrystallised from alcohol. Orange red prisms, m.p. 206–08° (decomp.), were obtained on slow crystallisation (0·2 g./kg. of plant material) (Found: C, 58·8; H, 5·5. $C_{20}H_{22}O_5NCl \cdot H_2O$ requires C, 58·6; H, 5·9%).

The red base.—The purified hydrochloride (0·8 g.) was dissolved in hot water and a dilute solution of sodium carbonate was added until alkaline, when the brown colour of the solution changed to blood red and on cooling, garnet red needles of the free alkaloid were obtained. It was recrystallised from alcohol to give the *red base* (0·6 g.), m.p. 206° (decomp.) (Found: C, 59·1; H, 6·1. $C_{20}H_{21}O_5N \cdot 3H_2O$ requires C, 58·7; H, 6·6%). The *nitrate* prepared by the usual method and crystallised from alcohol had m.p. 225° (decomp.). The *picrate* prepared by the usual method was crystallised from alcohol and had m.p. 210–11°.

Oxidation of the red base with potassium permanganate.—The red base (0·2 g.) on oxidation and working up in the usual way yielded hemipinic acid characterised as N-ethylhemipinimide, m.p. 90°.

Tetrahydro base—A solution of the red base hydrochloride (0·5 g.) in absolute alcohol (30 c.c.) containing platinum oxide (0·2 g.) was hydrogenated at 50 lb./sq. in. After the removal of solvent, *tetrahydrobase hydrochloride* was obtained as a yellow powder which crystallised from alcohol as yellow needles, m.p. 206° (Found: C, 61·0; H, 6·7. $C_{20}H_{24}O_4NCl \cdot H_2O$ requires C, 60·7; H, 6·5%).

The free tetrahydrobase was obtained by basification of the above hydrochloride with liquor ammonia and was crystallised from alcohol, as white

needles, m.p. 206–07° (Found: C, 70·7; H, 6·7; N, 4·1. $C_{20}H_{23}O_4N$ requires C, 70·5: H, 6·7; N, 4·1%).

O-Methyltetrahydrobase.—To a solution of the tetrahydrobase above (50 mg.) in absolute methanol (15 c.c.), a solution of diazomethane in ether (50 c.c.) (prepared from 5 g. of nitrosomethylurea) was added. Next day, the solvent was evaporated and the residue was crystallised from absolute ether to give *tetrahydropalmatine*, m.p. and mixed m.p. with an authentic specimen, 146° (Found: C, 70·8; H, 5·7. $C_{21}H_{25}O_4N$ requires C, 70·9; H, 6·0%).

O-Ethyl tetrahydrobase.—The tetrahydrobase (50 mg.) was ethylated in the same way as above using diazoethane. The product was crystallised from absolute ether, to give the ethyl ether as white needles, m.p. and mixed m.p. with *dl*-O-ethyltetrahydrojatrorrhizine (*see* below) 124°.

dl-*O-Ethyltetrahydrojatrorrhizine.*—*l*-Corypalmine (50 mg.) was ethylated in the same way as above using diazoethane. The product was dissolved in chloroform-methanol, treated with iodine in excess, and heated on a steam-bath with a little sodium acetate. The solvent and excess iodine were then removed and the residue treated on a steam-bath with zinc and dilute hydrochloric acid until all of it had dissolved to a colourless solution. An excess of ammonia was added and the liberated base extracted with ether and the ether extract evaporated. The residue was crystallised repeatedly from ether to give colourless needles melting at 124°.

Summary

Chemical investigation of the alkaloids of *Mahonia nepalensis* D.C. has established the identity of ' umbellatine ' with berberine and ' neprotine ' with jatrorrhizine.

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